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FTIR study of thermally induced magnetostructural transitions in breathing crystals

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Abstract

 "Breathing crystals" based on copper(II) hexafluoroacetylacetonates and pyrazolyl-substituted nitronyl nitroxides comprise the exchange-coupled clusters within the polymeric chains. Owing to an interplay of exchange interaction between copper(II) and nitroxide spins and Jahn-Teller nature of copper(II) complex, the breathing crystals demonstrate thermally and light-induced magnetostructural transitions in many aspects similar to the classical spin crossover. Herewith, we report the first application of variable temperature (VT) far/mid Fourier transform infrared (FTIR) spectroscopy and mid FTIR microscopy to breathing crystals. This VT-FTIR study was aimed toward clarification of the transitions mechanism previously debated on the basis of superconducting quantum interference device, X-ray diffraction, and electron paramagnetic resonance data. VT-FTIR showed the onset of new vibrational bands during phase transitions occurring at the expense of several existing ones, whose intensity was significantly reduced. The most pronounced spectral changes were assigned to corresponding vibrational modes using quantum chemical calculations. A clear-cut correlation was found between temperature-dependent effective magnetic moment of studied compounds and the observed VT-FTIR spectra. Importantly, VT-FTIR confirmed coexistence of two types of copper(II)-nitroxide clusters during gradual magnetostructural transition. Such clusters correspond to weakly coupled and strongly coupled spin states, whose relative contribution depends on temperature. The pronounced difference in the VT-FTIR spectra of two states in breathing crystals is a fingerprint of magnetostructural transition, and understanding of these characteristics achieved by us will be useful for future studies of breathing crystals as well as their diamagnetic analogues.

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